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(54) **HYBRID FIBER-REINFORCED PLASTIC**

FASERVERSTÄRKTER HYBRIDKUNSTSTOFF

COMPOSITE RENFORCE PAR DES FIBRES HYBRIDES

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(56) References cited:

| | |
|------------------------|-------------------------|
| EP-A- 0 062 973 | EP-A- 0 436 391 |
| JP-A- 3 042 242 | JP-A- 3 113 035 |
| JP-A- 3 199 011 | JP-A- 58 205 755 |
| US-A- 5 512 119 | |

- **DATABASE WPI Section Ch, Week 8403 Derwent Publications Ltd., London, GB; Class A12, AN 1984-013926 XP002149380 & JP 58 205755 A (MITSUBISHI RAYON CO LTD), 30 November 1983 (1983-11-30)**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 178 (M-1110), 8 May 1991 (1991-05-08) & JP 03 042242 A (TOYOBO CO LTD), 22 February 1991 (1991-02-22)**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 306 (C-0856), 6 August 1991 (1991-08-06) & JP 03 113035 A (KOBE STEEL LTD), 14 May 1991 (1991-05-14)**

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EP 0 927 628 B1

Description

[0001] The present invention relates to reinforced plastic members employing carbon fibre and high-elongation organic fibre; in particular, it relates to reinforced plastic members which, while being of light weight and high strength, are comparatively cheap and at the time of failure do not readily split apart or exhibit a dangerous mode of rupture and so are very safe when used for ski-poles, golf club shafts, bicycle frames, wheelchairs and the like.

[0002] Carbon fibre reinforced plastic members, with their outstanding characteristics of light weight, high strength and high modulus, are widely used for sporting goods and industrial structural materials. Hybrid prepregs having reinforcing carbon fibers and fibers of other materials are proposed in JP-A-58205755, US 5512119 and EP-A-0436391.

[0003] By using carbon fibre reinforced plastics it is possible to reduce the weight of members thereof in comparison to conventional materials, but carbon fibre reinforced plastics can exhibit a dangerous form of failure differing from that of conventional materials such as metals and, because of this, applications are either restricted or it may not be possible to fully manifest the outstanding characteristics of these materials in their applications.

[0004] For example, reducing the weight of ski-poles is of considerable significance but it is necessary that, should they break during use, the fracture surface presents no danger to the body. When conventional aluminium alloy ski-poles undergo failure, they mostly merely fold-over without breaking apart, but carbon fibre reinforced ski-poles which have become increasing popular in recent years comparatively frequently break apart when undergoing failure.

[0005] Furthermore, racing bicycle frames are another application where there is a strong demand for a reduction in weight and carbon fibre reinforced plastics are being used for this purpose. However, it is dangerous if, when the frame undergoes failure in an accident, it breaks apart and so it is desirable that even when undergoing failure that it does not break apart but remains intact.

[0006] Again, carbon fibre reinforced plastics are often used in order to reduce the weight of golf club shafts, but when the ground or a tree, etc, is struck as a result of a miss-hit, the situation may arise where the shaft snaps and the club head is sent flying. This is likely to be a particular problem when used by technically inexperienced children, and it is desirable that even when undergoing failure that it does not break apart but remains intact.

[0007] There are also many other applications such as wheel-chairs and badminton racquet shafts where a reduction in weight is desired and where it is also desired that those members with a strong possibility of coming into contact with the human body do not split apart should failure occur.

[0008] To deal with this problem in the case of ski-poles for example, a combination of glass fibre fabric or metal fibres with the carbon fibre reinforced plastic has been employed. However, such methods require the use of quite a large amount of glass fibre or metal fibre, so that the weight of the ski-pole increases or its rigidity is lowered and it becomes more difficult to use. Additionally, as well as high performance metal fibres being generally expensive, fabrication processability is poor and there is usually an increase in the cost of the ski-pole.

[0009] Again, in the case of bicycle frames and handle bars too, as described in Japanese Unexamined Patent Publication Nos 5-69874 and 5-147569, the method of incorporating, as reinforcing fibre, metal fibre and some fibre other than metal fibre for preventing breaking apart is also known. However, in such cases the problem also frequently arises of increased weight or raised cost.

[0010] The present invention seeks to resolve the aforesaid problem of the prior-art and offering, comparatively cheaply, fibre reinforced plastic members which, while retaining the outstanding characteristics of carbon fibre reinforced plastics of light weight and high strength, do not readily break apart at the time of failure or exhibit a dangerous failure mode, and so may be used safely as ski poles, bicycle frames, golf club shafts and the like.

[0011] Accordingly, in a first aspect the present invention provides a hybrid type fibre reinforced plastic which comprises carbon fibre and high-elongation organic fibre bundles, wherein, in cross section, bundles of high-elongation organic fibres are dispersed and the elongation at break of the high-elongation organic fibre is at least 10%.

[0012] In a second aspect the present invention provides a hybrid fibre reinforced plastic member which employs such a hybrid type fibre reinforced plastic. In a further aspect the present invention relates to a resin-impregnated hybrid prepreg which comprises carbon fibre and high-elongation organic fibre bundles impregnated with a resin, wherein, in cross section, bundles of high-elongation organic fibres are dispersed and the elongation at break of the high-elongation organic fibre is at least 10%. The invention also provides a method of producing a hybrid type fibre reinforced plastic, in which the fabrication is carried out using such a hybrid prepreg.

[0013] In a preferred embodiment, the high elongation organic fibre is dispersed, arranged in bundle form, with the percentage by volume thereof being 10 to 30% in terms of the carbon fibre.

Brief Explanation of the Drawings

[0014]

Figure 1 is an example of the cross-section of a member relating to the present invention.

Figure 2 is another example of the cross-section of a member relating to the present invention.

- 1 region having carbon fibre
- 2 region having high elongation organic fibre
- 3 hybrid region
- 4 non-hybrid region

Optimum Form for Practising the Invention

[0015] The hybrid type fibre reinforced plastic relating to the present invention is used for goods where there is a fear of dangerous breakdown, for example it is used for all of a ski pole or golf club shaft, etc or for a member thereof. Where required, it may also be one portion of a fibre reinforced plastic.

[0016] The carbon fibre employed may be of any kind, such as polyacrylonitrile-based or pitch-based carbon fibre, including so-called graphite fibre, but a polyacrylonitrile-based carbon fibre with high tensile strength is preferred. With regard to the form thereof, there can be used twisted yarn, de-twisted yarn or non-twisted yarn, but de-twisted yarn or non-twisted yarn is preferred in terms of the balance between the member fabrication properties and strength.

[0017] The high elongation organic fibre should have a tensile elongation at break higher than that of glass fibre which is the typical inorganic fibre. Specific examples are polyamide fibre, polyester fibre, polyvinyl alcohol fibre, polyacrylonitrile fibre and polyurethane fibre. Of these, polyester fibre and polyamide fibre are preferred in that, as well as having a high tensile elongation at break, such fibre is comparatively cheap and is outstanding in its handling properties. At the time of member failure, that is to say when the carbon fibre breaks, the high elongation organic fibre does not break at the same time, and by sufficient absorption of the accumulated strain energy, the splitting apart of the member and exposure of a dangerous fracture surface are avoided. Consequently, the appropriate high elongation organic fibre is one with a high tensile strength and high tensile elongation at break, and it is preferred that it has a high residual energy absorption level following, for example, 5% tensile strain. The tensile strength is preferably at least 0.5 N/tex and the tensile elongation at break, which is especially important, is preferably from 10 to 200%, with from 15 to 50% further preferred.

[0018] Where the carbon fibre and the high elongation organic fibre are uni-directionally aligned, the effects are striking, but there is no need, where there are production limitations or the like, for the alignment necessarily to match perfectly. However, it is preferred that the difference in direction of the two be within 3°.

[0019] As well as the carbon fibre and the high elongation organic fibre, there may also be included a third fibre within a range such that the effects of the invention are not lost. In terms of achieving a balance between the mechanical properties of the member and production stability, the fibre volume fraction, containing all fibre, is preferably within the range 40 to 80% and still more preferably within the range 50 to 70%.

[0020] As the matrix resin, there can be used various types of thermosetting resin and thermoplastic resin, such as epoxy resins, phenolic resins, polyester resins and vinyl ester resins. Of these, epoxy resins are preferred in that fabrication is easy and their properties excellent. Again, for the purposes of adding various properties and functions, particulate and fibre-form materials may be included in the matrix resin within a range such that the effects of the invention are not lost.

[0021] The alignment direction of the carbon fibre and the high elongation organic fibre is preferably parallel to the principal axis of the member. The principal axis of the member corresponds to the axis which most readily undergoes failure, and in the case of a sheet-form, rod-form or tubular member it is the axis in the longitudinal direction. Where the fibre is aligned with the principal axis of the member, it is possible to prevent more effectively the occurrence of splitting apart along with failure of the member and the exposure of a fracture surface.

[0022] There are no particular restrictions as to the arrangement of the carbon fibre and the high elongation organic fibre in the hybrid regions, but in order to prevent overall failure of the member it is preferred that, in the cross-section perpendicular to the alignment direction of the fibre, high elongation organic fibre bundles are dispersed and arranged within regions having the carbon fibre, in a so-called 'sea/islands' structure. In the case of a tubular member, this structure preferably has a cross-section as shown for example in Figure 1, where the high elongation organic fibre bundle regions 2 are dispersed and arranged within the region 1 with the carbon fibre. Now, in the figure, 3 denotes the hybrid region. In this way, it is possible to prevent simultaneous rupture of the carbon fibre and high elongation organic fibre, and it is also possible to retain uniformity of the properties as a whole. Again, at the same time, it is also possible to suppress the effects, on the properties of the member, in cases where debonding occurs between the region with the carbon fibre and the high elongation organic fibre bundle regions. With this kind of arrangement, it is preferred that the mutual separation between the regions of high elongation organic fibre does not exceed 5 mm in the case of members of the size of ski poles, golf club shafts and bicycle frames. Again, by using high elongation organic fibre which has been treated with a release agent or which is in a non-adhered state, it is also possible to prevent still more effectively overall failure of the member.

[0023] Furthermore, the percentage by volume of high elongation organic fibre in terms of the carbon fibre preferably does not exceed 30%. If it lies above this range, strength and rigidity tend to be lowered. On the other hand in a case like that of a golf club shaft, which is relatively light and where there are relatively few hybrid regions, it is more preferably at least 10%.

5 [0024] The hybrid type fibre reinforced plastic of the present invention can, where required, be used in combination with various kinds of fibre reinforced plastic or metal, etc. For example, Figure 2 shows a tubular material with a cross-section in which there is a non-hybrid region 4 on the inside. Preferably, of the fibre reinforced plastic portion having carbon fibre aligned in parallel to the principal axis of the member, a portion exceeding 50 vol% and more preferably exceeding 80 vol% should be a hybrid region.

10 [0025] The member of the present invention can have any shape such as a sheet form or rod form, depending on the particular application and structure, but a tubular shape is preferred in order to make the most of the characteristics of the carbon fibre reinforced plastic and to enhance the effects of the invention. Tubular shape means a shape of substantially circular cross-section which is hollow or which has a different material such as a foam material in the interior and, where required, the principal axis may be curved or a taper can be provided.

15 [0026] Moreover, a structure having high-elongation fibre covering carbon fibre bundles also prevents splitting apart and the scatter of fragments at the time of failure of the member and is effective in enhancing safety. With this structure, the high elongation organic fibre need not be aligned in the same direction as the carbon fibre, and the covering may be carried out for example with the high elongation organic fibre running around the circumference of the carbon fibre bundle in helical fashion. Now, in the cross-section perpendicular to the alignment direction of the carbon fibre, it is preferred that a region exceeding 40% of the respective peripheries of the carbon fibre bundles be covered with high elongation carbon fibre. In the case of this structure too, the form of the member is preferably tubular.

20 [0027] Ski poles comprising a tubular member of the present invention do not produce an exposed fracture surface when they break during use, and there is little possibility of causing harm to the body, so they have markedly higher safety when compared to conventional carbon fibre reinforced plastic ski poles. It is possible to provide ski poles which do not undergo splitting failure due to a compressive buckling force in the ski pole buckling point test specified in JIS S7026. With regard to the light weight, strength and appropriate rigidity which are the important characteristics of a ski pole, there is very little difference when compared to conventional carbon fibre reinforced plastic ski poles, and practically no difference can be felt at the time of use.

25 [0028] Besides ski poles, the member of the present invention is ideal for use in other applications where a reduction in weight is desired and where it is desired that the failure mode, should failure occur, pose little danger to the body, such as golf club shafts, bicycle frames, wheelchair frames, hockey sticks, badminton rackets, kendo fencing equipment, fishing rods and walking aids.

30 [0029] The hybrid type fibre reinforced plastic of the present invention can be fabricated using a hybrid prepreg comprising uni-directionally aligned carbon fibre and high elongation organic fibre impregnated with resin. The hybrid prepreg is obtained by a method such as producing a uni-directionally aligned sheet-form of the carbon fibre and high elongation organic fibre, then impregnating this with a resin prior to hardening, or alternatively affixing the high elongation organic fibre to the surface of a known carbon fibre prepreg. For fully manifesting the performance of the fibre reinforced plastic member of the present invention, it will be appropriate if the volume fraction of high elongation organic fibre in terms of the carbon fibre in the hybrid prepreg does not exceed 50%. This hybrid prepreg can also be used by, for example, affixing a separate prepreg comprising aligned carbon fibre in sheet form, and as the fibre in the affixed prepreg there may be used fibre of different strength or modulus, or there may be used different fibre such as glass fibre or aramid fibre. Again, it is possible to adjust the high elongation fibre content by adjusting the amount of affixed prepreg.

35 [0030] With regard to the aligned high elongation organic fibre, by arranging this at intervals in the direction perpendicular to the fibre direction, when the fibre reinforced plastic member of the present invention is fabricated, regions with high elongation organic fibre are dispersed and arranged and can be employed advantageously. Again, as stated above, it is better if the mutual apacing between high elongation organic fibre regions within the member is not too great, so it will be appropriate in the present invention if the spacing between high elongation organic fibre regions, that is to say the 'pitch', does not exceed 50 mm. Moreover, where it does not exceed 30 mm, and still more preferably where it does not exceed 20 mm, the capacity of the hybrid type fibre reinforced plastic can be fully manifested.

40 [0031] The member of the present invention can be produced by a process practically no different from that of conventional carbon fibre reinforced plastic members, by fabrication using a hybrid prepreg comprising uni-directionally aligned carbon fibre and high elongation organic fibre impregnated with resin. Consequently, the production costs are practically no different from hitherto.

45 [0032] Below, explanation is given by providing some examples and comparative examples. An outline of the results obtained in these is shown in Table 1 towards the end.

Example 1

[0033] Carbon fibre prepreg A (prepreg weight per unit area 320 g/m², fibre content 67 wt%) was prepared by impregnating, with B-stage epoxy, PAN-based carbon fibre bundles (number of filaments 12000, thickness 804 tex, elongation 2.1%, tensile strength 4900 MPa, and tensile modulus 230 GPa) which had been aligned and laid out in the form of a sheet.

[0034] Identical PAN-based carbon fibre bundles and nylon 66 fibre bundles (number of filaments 306, thickness 210 tex, elongation 19.5%, tensile strength 0.93 N/tex) were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 bundles at this time was made 30 mm. Hybrid prepreg B (prepreg weight per unit area 315 g/m², fibre content 68 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of nylon 66 in terms of the carbon fibre in hybrid prepreg B was 5%.

[0035] Firstly, carbon fibre prepreg A was wrapped around a release agent-treated stainless steel mandrel of outer diameter 8 mm on the narrower diameter side and 11 mm on the wider diameter side, and of length 1400 mm, in such a way that the fibre direction was perpendicular to the principal axis of the mandrel, then the hybrid prepreg B was wrapped around in such a way that fibre direction was parallel to the principal axis of the mandrel, after which, by the method normally conducted by those skilled in the art, wrapping tape was wound around, and curing carried out in an electric oven, after which the mandrel was removed, the outer diameter polished and the two ends cut off, to produce a shaft for a ski pole of length 1250 mm.

[0036] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which the regions having nylon 66 were dispersed in the region having carbon fibre. The wall thickness of the shaft was 1.5 mm.

[0037] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 690 N. While there was some scatter of small fragments at the time of failure, there was no breaking apart of the shaft.

Example 2

[0038] PAN-based carbon fibre bundles and nylon 66 fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 fibre bundles at this time was made 15 mm. Hybrid prepreg C (prepreg weight per unit area 311 g/m², fibre content 68 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the nylon 66 fibre in terms of the carbon fibre in hybrid prepreg C was 10%.

[0039] A shaft for a ski pole was produced in the same way as in Example 1 except that there was used hybrid prepreg C instead of hybrid prepreg B.

[0040] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which regions having nylon 66 fibre were dispersed in the region having carbon fibre. The wall thickness of the shaft was 1.5 mm.

[0041] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 688 N. There was no scattering of fragments at the time of failure and there was no breaking apart of the shaft.

Example 3

[0042] PAN-based carbon fibre bundles and nylon 66 fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 fibre bundles at this time was made 5 mm. Hybrid prepreg D (prepreg weight per unit area 296 g/m², fibre content 66 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the nylon 66 fibre in terms of the carbon fibre in this hybrid prepreg D was 29%.

[0043] A shaft for a ski pole was produced in the same way as in Example 1 except that there was used hybrid prepreg D instead of hybrid prepreg B.

[0044] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which regions having nylon 66 fibre were dispersed in the region having carbon fibre. The wall thickness of the shaft was 1.5 mm.

[0045] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 620 N. There was no scatter of broken fragments at the time of failure and there was no breaking apart of the shaft.

Example 4

[0046] PAN-based carbon fibre bundles identical to those used in Example 1 and polyester fibre bundles (number of filaments 360, thickness 167 tex, elongation 11.8%, tensile strength 0.77 N/tex) were uni-directionally aligned and laid out in the form of a sheet. The pitch between the polyester fibre bundles at this time was made 10 mm. Hybrid prepreg E (prepreg weight per unit area 314 g/m², fibre content 68 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the polyester fibre in terms of the carbon fibre in this hybrid prepreg E was 10%.

[0047] A shaft for a ski pole was produced in the same way as in Example 1 except that there was used hybrid prepreg E instead of hybrid prepreg B.

[0048] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which regions having polyester fibre were dispersed in the region having carbon fibre. The wall thickness of the shaft was 1.5 mm.

[0049] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 660 N. There was no scattering of fragments at the time of failure and there was no breaking apart of the shaft.

Example 5

[0050] Covered yarn comprising a PAN based carbon fibre bundle identical to that used in Example 1 covered in helical fashion with a nylon 66 fibre bundle was aligned and laid out in the form of a sheet. Hybrid prepreg F (prepreg weight per unit area 300 g/m², fibre content 67 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the nylon in terms of the carbon fibre in this covered yarn prepreg F was 15%.

[0051] A shaft for a ski pole was produced in the same way as in Example 1 except that there was used covered yarn prepreg F instead of hybrid prepreg B.

[0052] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the region on the shaft exterior where the carbon fibre direction was parallel to the principal axis had a structure with 50% of the circumference of each carbon fibre bundle covered with a nylon 66 bundle. The wall thickness of the shaft was 1.5 mm.

[0053] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 670 N. There was no scattering of broken fragments at the time of failure and there was no breaking apart of the shaft.

Comparative Example 1

[0054] A shaft for a ski pole was produced in the same way as in Example 1 except that carbon fibre prepreg A was used instead of the hybrid prepreg B.

[0055] At the end face of this shaft, the shaft wall thickness was 1.5 mm.

[0056] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 690 N. Broken fragments were scattered at the time of failure, there was breaking apart of the shaft and, furthermore, the fracture surface had a finely split state, so dangerous failure was exhibited.

Comparative Example 2

[0057] Nylon 66 fibre bundles identical to those used in Example 1 were aligned and laid out in the form of a sheet. Nylon prepreg G (prepreg weight per unit area 239 g/m², fibre content 58 wt%) was prepared by impregnating this with B-stage epoxy resin.

[0058] A shaft for a ski pole was produced in the same way as in Example 1 except that nylon prepreg G was used instead of the hybrid prepreg B.

[0059] At the end face of this shaft, the shaft wall thickness was 1.5 mm.

[0060] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 35 N. There was no scattering of broken fragments at the time of failure and there was no breaking apart of the shaft.

Example 6

[0061] PAN-based carbon fibre bundles identical to those used in Example 1 were aligned and laid out in the form of a sheet, which was impregnated with B-stage epoxy resin to prepare carbon fibre prepreg H (prepreg weight per unit area 88 g/m², fibre content 63 wt%).

[0062] Identical PAN-based carbon fibre bundles and nylon 66 fibre bundles identical to those used in Example 1

were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 fibre bundles at this time was made 10 mm. Hybrid prepreg I (prepreg weight per unit area 261 g/m², fibre content 70 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the nylon 66 in terms of the carbon fibre in this hybrid prepreg I was 21%.

5 [0063] E-glass fibre bundles (number of filaments 2000, thickness 110 tex, elongation 4%, tensile strength 2500 MPa, and tensile modulus 75 GPa) were formed into a cloth form in plain-weave fashion (GF yarn count; warp yarns = 39 per inch and weft yarns = 39 per inch) and laid out in the form of a sheet, which was impregnated with B-stage epoxy resin to prepare a glass cloth prepreg J (prepreg weight per unit area 133 g/m², fibre content 52 wt%).

10 [0064] Firstly, the carbon fibre prepreg H was wound around a release agent-treated stainless steel mandrel of outer diameter 5 mm on the narrower diameter side and 13 mm on the wider diameter side, and of length 1400 mm, in such a way that the fibre direction was at an angle of about $\pm 45^\circ$ to the principal axis of the mandrel, then the hybrid prepreg I was wound around in such a way that fibre direction was roughly parallel to the principal axis of the mandrel, after which, glass cloth prepreg J was wrapped around. Next, by the method normally conducted by those skilled in the art, wrapping tape was wound around and curing carried out in an electric oven, after which the mandrel was removed,

15 the outer diameter polished and the two ends cut off, to produce a shaft for a ski pole of length 1120 mm. [0065] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which the regions having nylon 66 were dispersed in the region having carbon fibre. The wall thickness of the shaft was 1.5 mm.

20 [0066] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 640 N. There was no scattering of broken fragments at the time of failure and there was no breaking apart of the shaft.

Example 7

25 [0067] PAN-based carbon fibre bundles and nylon 66 fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 fibre bundles at this time was made 7.5 mm. Hybrid prepreg K (prepreg weight per unit area 214 g/m², fibre content 63 wt%) was prepared by impregnating this with B-stage epoxy resin. The percentage by volume of the nylon 66 fibre in terms of the carbon fibre in this hybrid prepreg K was 41%.

30 [0068] A shaft for a ski pole was produced in the same way as in Example 6 except that there was used hybrid prepreg K instead of hybrid prepreg I.

[0069] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which regions having nylon 66 fibre were dispersed in the region having carbon fibre. The wall thickness

35 of the shaft was 1.5 mm. [0070] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 510 N. There was no scattering of broken fragments at the time of failure and there was no breaking apart of the shaft.

Comparative Example 3

40 [0071] PAN-based carbon fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet, which was impregnated with B-stage epoxy resin to prepare carbon fibre prepreg L (prepreg weight per unit area 261 g/m², fibre content 67 wt%).

45 [0072] A shaft for a ski pole was produced in the same way as in Example 6 except that there was used carbon fibre prepreg L instead of hybrid prepreg I. The wall thickness of the shaft was 1.5 mm.

[0073] When this shaft was subjected to a buckling point test based on JIS S7026, the maximum load was 660 N. Broken fragments were scattered at the time of failure, there was breaking apart of the shaft and, furthermore, the fracture surface had a finely split state, so dangerous failure was exhibited.

50 Example 8

[0074] PAN-based carbon fibre bundles and nylon 66 fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet. The pitch between the nylon 66 fibre bundles at this time was made 14.5 mm. Hybrid prepreg M (prepreg weight per unit area 187 g/m², fibre content 68 wt%) was prepared by

55 impregnating this with B-stage epoxy resin. The percentage by volume of the nylon 66 fibre in terms of the carbon fibre in this hybrid prepreg K was 21%. [0075] PAN-based carbon fibre bundles (number of filaments 6000, thickness 225 tex, elongation 1.2%, tensile strength 4410 MPa and tensile elastic modulus 375 GPa) were aligned and laid out in the form of a sheet, which was

impregnated with B-stage epoxy resin to prepare carbon fibre prepreg N (prepreg weight per unit area 174 g/m², fibre content 67 wt%).

5 [0076] Firstly, the carbon fibre prepreg N was wound around a release agent-treated stainless steel mandrel of outer diameter 5.4 mm on the narrower diameter side and 14 mm on the wider diameter side, and of length 1400 mm, in such a way that the fibre direction was at an angle of about $\pm 45^\circ$ to the principal axis of the mandrel, then the hybrid prepreg M was wound around in such a way that fibre direction was roughly parallel to the principal axis of the mandrel, after which hybrid prepreg M was wound around as a tip reinforcement on the narrower diameter side. Next, by the method normally conducted by those skilled in the art, wrapping tape was wound around and curing carried out in an electric oven, after which the mandrel was removed, the outer diameter polished and the two ends cut off, to produce
10 a shaft for a golf club of length 1143 mm.

[0077] When the end faces of this shaft were polished and observed with an optical microscope, it was seen that the hybrid region on the shaft exterior where the fibre direction was parallel to the principal axis had a sea/islands structure in which the regions having nylon 56 were dispersed in the region having carbon fibre. The wall thickness of the shaft in the region without the tip reinforcement was 0.8 mm.

15 [0078] When this shaft was subjected to a three-point bending test at a span of 600 mm, the maximum load was 340 N. There was no scattering of broken fragments at the time of failure and there was no breaking apart of the shaft.

Comparative Example 4

20 [0079] PAN-based carbon fibre bundles identical to those used in Example 1 were uni-directionally aligned and laid out in the form of a sheet, which was impregnated with B-stage epoxy resin to prepare carbon fibre prepreg O (prepreg weight per unit area 187 g/m², fibre content 67 wt%).

[0080] A shaft for a golf club was produced in the same way as in Example 8 except that there was used carbon fibre prepreg O instead of hybrid prepreg M. The wall thickness of the shaft in the region without the tip reinforcement
25 was 0.8 mm.

[0081] When this shaft was subjected to a three-point bending test at a span of 600 mm, the maximum load was 350 N. At the time of failure there was a breaking apart of the shaft and scattering.

Industrial Applicability

30 [0082] Fibre reinforced plastic members of the present invention either have hybrid regions having both carbon fibre and high-elongation organic fibre, or have aligned carbon fibre bundles with high-elongation organic fibre covering them, and so, while maintaining the outstanding characteristics of carbon fibre reinforced plastics of light weight and high strength, they do not readily split apart at the time of failure or exhibit a dangerous failure mode, so it is possible
35 to offer highly safe members at low cost.

[0083] The members of the present invention can be suitably used as ski poles, bicycle frames, golf club shafts, badminton racket shafts, wheelchair frames or hockey sticks, etc.

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Table 1

| | Nylon Filare 1) | | Prepreg | | Shaft Internal Diameter / \varnothing_{90} Thickness (mm/mm) | Maximum Load (N) | Safety at time of Failure |
|-----------|----------------------|---------------------|--|----------------------------|--|------------------------|---|
| | Percent by Volume | Pitch (mm) | Weight per Unit Area (g/m ²) | Weight Percent of fibre | | | |
| Example 1 | 5 | 30 | 315 | 63 | 11/1.5 | 690 | did not break apart but scatter of small fragments |
| Example 2 | 10 | 15 | 311 | 68 | 11/1.5 | 688 | did not break apart, no scatter of fragments |
| Example 3 | 29 | 5 | 296 | 66 | 11/1.5 | 620 | did not break apart, no scatter of fragments |
| Example 4 | 10 | 10 | 314 | 68 | 11/1.5 | 660 | did not break apart, no scatter of fragments |
| Example 5 | 15 | helical covering | 300 | 67 | 11/1.5 | 670 | did not break apart, no scatter of fragments |
| Example 6 | 21 | 10 | 261 | 70 | 13/1.5 | 640 | did not break apart, no scatter of fragments |
| Example 7 | 41 | 7.5 | 214 | 63 | layered with different prepreg 13/1.5 | 510 | did not break apart, no scatter of fragments |
| Example 8 | 21 | 14.5 | 187 | 68 | layered with different prepreg 14/0.8 | 340 | did not break apart, no scatter of fragments |
| Comp.Ex.1 | - | - | 320 | 67 | layered with different prepreg 11/1.5 | 690 | breaks apart, scatter of fragments, dangerous fracture surface |
| Comp.Ex.2 | ∞ | 0 | 239 | 58 | 11/1.5 | 35 | did not break apart, no scatter of fragments |
| Comp.Ex.3 | - | - | 261 | 67 | 13/0.5 | 660 | breaks apart, scatter of fragments, dangerous fracture surface |
| Comp.Ex.4 | - | - | 187 | 67 | layered with different prepreg 14/0.8 | 350 | breaks apart, scatter of fragments |

Note: 1) Number of filaments = 306, thickness 210 tex;
except in Example 4 where polyester fibre bundles used, number of filaments = 360, thickness 167 tex

Claims

1. A hybrid type fibre reinforced plastic which comprises carbon fibre and high-elongation organic fiber bundles, wherein , in cross section, bundles of high-elongation organic fibres are dispersed and the elongation at break of the high-elongation organic fibre is at least 10%. 5
2. A hybrid type fibre reinforced plastic according to Claim 1, in which the thickness of the high-elongation organic fibre bundle is from 40 to 300 tex.
3. A hybrid type fibre reinforced plastic according to Claim 2, in which the thickness of the high-elongation organic fibre bundle is from 180 to 300 tex. 10
4. A hybrid type fibre reinforced plastic according to Claim 1, in which the high-elongation organic fibre is a polyamide fibre. 15
5. A hybrid type fibre reinforced plastic according to any one of Claims 1 to 4, in which carbon fibre and high-elongation organic fibre bundles are uni-directionally aligned.
6. A hybrid type fibre reinforced plastic according to Claim 1, in which high-elongation organic fibre bundle regions are dispersed and arranged, in cross section, within regions having carbon fibres. 20
7. A hybrid type fibre reinforced plastic according to Claim 1, in which the proportion by volume of the high-elongation organic fibre in terms of the carbon fibre is from 10 to 30%.
8. A hybrid type fibre reinforced plastic according to Claim 1, in which the elongation at break of the high-elongation organic fibre is 15 - 50%. 25
9. A hybrid type fibre reinforced plastic according to Claim 1, in which high-elongation organic fibre covers a carbon fibre bundle. 30
10. A hybrid type fibre reinforced plastic according to Claim 1, in which the high-elongation organic fibre is treated with a release agent.
11. A hybrid type fibre reinforced plastic according to Claim 1, in which the high elongation organic fibre bundles are incorporated in a non-adhered state. 35
12. A hybrid type fibre reinforced plastic member employing the hybrid type fibre reinforced plastic as claimed in any one of Claims 1 to 11.
13. A hybrid type fibre reinforced plastic member according to Claim 12, in which the alignment direction of the carbon fibre and the high-elongation organic fibre bundle is parallel to the principal axis thereof. 40
14. A hybrid type fibre reinforced plastic member according to Claim 12, which is of tubular shape.
15. A ski pole having a hybrid type fibre reinforced plastic member as claimed in Claim 12. 45
16. A shaft for a golf club having a hybrid type fibre reinforced plastic member as claimed in Claim 12.
17. A hybrid prepreg which comprises carbon fibre and high-elongation organic fibre bundles impregnated with a resin, wherein, in cross section, bundles of high-elongation organic fibres are dispersed and the elongation at break of the high-elongation organic fibre is at least 10%. 50
18. A hybrid prepreg according to Claim 17, in which the proportion by volume of the high-elongation organic fibre in terms of the carbon fibre is 10 - 50%. 55
19. A hybrid prepreg according to Claim 17, in which high-elongation organic fibre bundles are arranged at a pitch at right angles to the fibre axis.

20. A hybrid prepreg according to Claim 19, in which high-elongation organic fibre bundles are arranged at a pitch of no more than 50 mm.
21. A method of producing a hybrid type fibre reinforced plastic which is characterized in that fabrication is carried out using hybrid prepreg according to Claim 17.

Patentansprüche

1. Faserverstärkter Hybridkunststoff, welcher eine Kohlefaser und dehnfähige, organische Faserbündel umfasst, worin die Bündel aus dehnfähigen, organischen Fasern im Querschnitt verteilt sind und die Bruchdehnung der dehnfähigen, organischen Fasern zumindest 10 % beträgt.
2. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die Dicke des dehnfähigen, organischen Faserbündels 40 bis 300 tex beträgt.
3. Faserverstärkter Hybridkunststoff nach Anspruch 2, in welchem die Dicke des dehnfähigen, organischen Faserbündels 180 bis 300 tex beträgt.
4. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die dehnfähige, organische Faser eine Polyamidfaser ist.
5. Faserverstärkter Hybridkunststoff nach einem der Ansprüche 1 bis 4, in welchem eine Kohlefaser und dehnfähige, organische Faserbündel in dieselbe Richtung ausgerichtet sind.
6. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem Bereiche aus dehnfähigen, organischen Faserbündeln im Querschnitt verteilt und innerhalb von Bereichen mit Kohlefasern angeordnet sind.
7. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem der Volumsanteil der dehnfähigen, organischen Fasern, bezogen auf die Kohlefasern, 10 bis 30 % beträgt.
8. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die Bruchdehnung der dehnfähigen, organischen Fasern 15 bis 50 % beträgt.
9. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die dehnfähigen, organischen Fasern ein Kohlefaserbündel bedecken.
10. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die dehnfähigen, organischen Fasern mit einem Gleitmittel behandelt sind.
11. Faserverstärkter Hybridkunststoff nach Anspruch 1, in welchem die dehnfähigen, organischen Faserbündel in einem nichthaftenden Zustand eingearbeitet sind.
12. Faserverstärkter Hybridkunststoff-Bauteil, in dem faserverstärkter Hybridkunststoff nach einem der Ansprüche 1 bis 11 verwendet wird.
13. Faserverstärkter Hybridkunststoff-Bauteil nach Anspruch 12, in dem die Ausrichtung der Kohlefasern und des dehnfähigen, organischen Faserbündels parallel zu seiner Hauptachse ist.
14. Faserverstärkter Hybridkunststoff-Bauteil nach Anspruch 12, der röhrenförmig ist.
15. Skistock mit einem faserverstärkten Hybridkunststoff-Bauteil nach Anspruch 12.
16. Schaft für einen Golfschläger mit einem faserverstärkten Hybridkunststoff-Bauteil nach Anspruch 12.
17. Hybridprepreg, welches Kohlefasern und mit einem Harz imprägnierte, dehnfähige, organische Faserbündel umfasst, worin die Bündel aus dehnfähigen, organischen Fasern im Querschnitt verteilt sind und die Bruchdehnung der dehnfähigen, organischen Fasern zumindest 10 % beträgt.

18. Hybridpreg nach Anspruch 17, in welchem der Volumsanteil der dehnfähigen, organischen Fasern, bezogen auf die Kohlefasern, 10 bis 50 % beträgt.
19. Hybridpreg nach Anspruch 17, in welchem dehnfähige, organische Faserbündel in einem Abstand im rechten Winkel zur Faserachse angeordnet sind.
20. Hybridpreg nach Anspruch 19, in welchem dehnfähige, organische Faserbündel in einem Abstand von nicht mehr als 50 mm angeordnet sind.
21. Verfahren zur Herstellung eines faserverstärkten Hybridkunststoffes, **dadurch gekennzeichnet, dass die Fabrikation unter Verwendung eines Hybridpregs nach Anspruch 17 durchgeführt wird.**

Revendications

1. Matière plastique renforcée par des fibres du type hybride, comprenant des faisceaux de fibres de carbone et de fibres organiques à allongement élevé, dans laquelle, en coupe transversale, des faisceaux de fibres organiques à allongement élevé sont dispersés et l'allongement à la rupture de la fibre organique à allongement élevé est d'au moins 10%.
2. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle l'épaisseur du faisceau de fibres organiques à allongement élevé est comprise entre 40 et 300 tex.
3. Matière plastique renforcée par des fibres du type hybride selon la revendication 2, dans laquelle l'épaisseur du faisceau de fibres organiques à allongement élevé est comprise entre 180 et 300 tex.
4. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle la fibre organique à allongement élevé est une fibre de polyamide.
5. Matière plastique renforcée par des fibres du type hybride selon l'une quelconque des revendications 1 à 4, dans laquelle les faisceaux de fibres de carbone et de fibres organiques à allongement élevé sont alignés de manière unidirectionnelle.
6. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle les régions de faisceaux de fibres organiques à allongement élevé sont dispersées et disposées, en coupe transversale, à l'intérieur des régions ayant des fibres de carbone.
7. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle la proportion en volume de la fibre organique à allongement élevé par rapport à la fibre de carbone est comprise entre 10 et 30%.
8. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle l'allongement à la rupture de la fibre organique à allongement élevé est compris entre 15 et 50%.
9. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle la fibre organique à allongement élevé recouvre un faisceau de fibres de carbone.
10. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle la fibre organique à allongement élevé est traitée avec un agent anti-adhésif.
11. Matière plastique renforcée par des fibres du type hybride selon la revendication 1, dans laquelle les faisceaux de fibres organiques à allongement élevé sont incorporés dans un état non adhérent.
12. Élément en matière plastique renforcée par des fibres du type hybride utilisant la matière plastique renforcée par des fibres du type hybride selon l'une quelconque des revendications 1 à 11.
13. Élément en matière plastique renforcée par des fibres du type hybride selon la revendication 12, dans lequel la direction d'alignement de la fibre de carbone et du faisceau de fibres organiques à allongement élevé est parallèle à l'axe principal de celui-ci.

14. Elément en matière plastique renforcée par des fibres du type hybride selon la revendication 12, qui est de forme tubulaire.
- 5 15. Bâton de ski ayant un élément en matière plastique renforcée par des fibres du type hybride selon la revendication 12.
16. Tige pour canne de golf ayant un élément en matière plastique renforcée par des fibres du type hybride selon la revendication 12.
- 10 17. Préimprégné hybride comprenant des faisceaux de fibres de carbone et de fibres organiques à allongement élevé imprégnés d'une résine, dans lequel, en coupe transversale, les faisceaux de fibres organiques à allongement élevé sont dispersés et l'allongement à la rupture de la fibre organique à allongement élevé est d'au moins 10%.
- 15 18. Préimprégné hybride selon la revendication 17, dans lequel la proportion en volume de la fibre organique à allongement élevé par rapport à la fibre de carbone est comprise entre 10 et 50%.
19. Préimprégné hybride selon la revendication 17, dans lequel les faisceaux de fibres organiques à allongement élevé sont agencés suivant un pas formant un angle droit avec l'axe de la fibre.
- 20 20. Préimprégné hybride selon la revendication 19, dans lequel les faisceaux de fibres organiques à allongement élevé sont agencés suivant un pas non supérieur à 50 mm.
- 25 21. Procédé de production d'une matière plastique renforcée par des fibres du type hybride, caractérisé en ce que la fabrication est effectuée en utilisant le préimprégné hybride selon la revendication 17.

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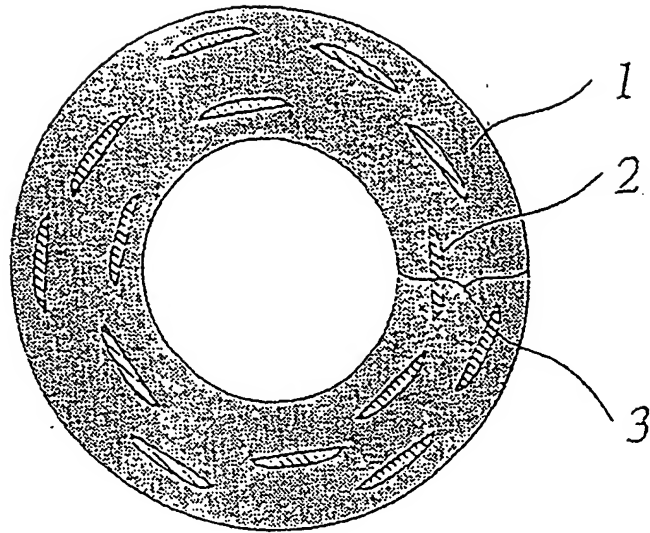


Fig. 1

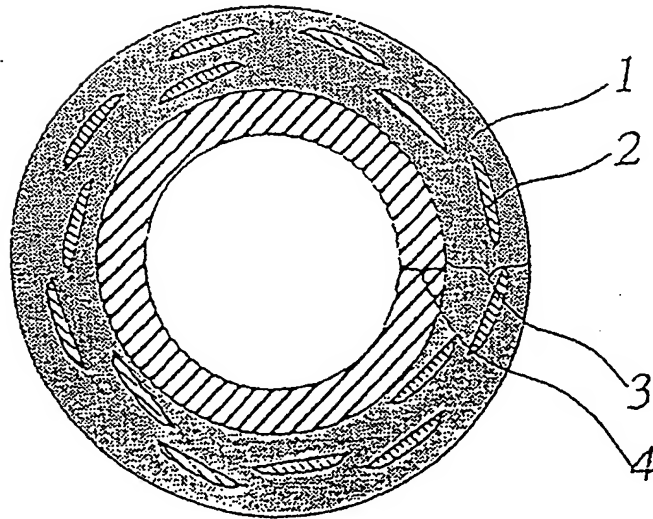


Fig. 2